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Fabrication and Characterization of CuO Nanofibers using Nanofiber Generator

R. G. Sethuraman[1], T. Venkatachalam[2*], E. P. Subramaniam[3], T. V. Viknesh[4], V. Manikandan[5]

[1]*Department of Physics, Kumaraguru College of Technology, Coimbatore, TN, India.*
[*2]*Department of Physics, Coimbatore Institute of Technology, Coimbatore,TN, India.*
[3]*Department of Chemistry, Coimbatore Institute of Technology, Coimbatore, TN, India.*
[4,5]*Department of Electrical & Electronics Engineering, Coimbatore Institute of Technology, Coimbatore, TN, India.*

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Abstract

Improvised electro-spin coating unit was designed, fabricated and optimized to fabricate nano-fibers. Composite nano fibers of CuO (dissolved in PVA) were fabricated using this unit. The prepared fibers were annealed at three different temperatures (400 °C, 500 °C and 600 °C) using muffle furnace, all the continuous fibers were broken down to nano crystals. The structural and composition of the nano crystals were analyzed using XRD and EDAX measurements. The X-ray diffraction peaks revealed that the crystals are monoclinic crystalline structure. The composition of the crystal is confirmed as CuO from the percentage of constituents of Copper and Oxygen in EADX results. The optical properties of the fibers were studied by using spectrophotometer. The optical band gap energy is found to be nearly 2 eV. The surface morphology of the crystal was studied using FESEM analysis. The crystals are found to be defect free and they are excellent material for high sensitive optoelectronic sensors.

Keywords: *Band gap; CuO; EDAX; FESEM; Monoclinic crystal; Nano crystals; Nano fiber; Nano fiber generator; Optoelectronic sensors; XRD.*

1. INTRODUCTION

In recent years, nano structured metal oxide materials have been proven as milestone in modern electronic products. They exhibit excellent electronic, optical, mechanical properties and many more for all the intelligent systems including embedded systems. Among metal oxides, transition metal oxides, specifically Copper (II) Oxide (CuO) is a well known semiconductor (P type) with a band gap of 2.0 eV. It also has a wide range of applications such as optoelectronic sensors (Mathews *et al*. 2010), gas sensors (Zhang *et al*. 2009; Duc *et al*. 2014), high-Tc superconductors, magnetic storage devices, catalyst (Jun *et al*. 2009), antioxidant photo electrical, photo thermal, antibacterial (Torres *et al*. 2010), etc. Various methods such as thermal methods, chemical methods, electrochemical method, hydrothermal method, decomposition method, etc. were adopted for fabrication of nano crystals. In this research, electro spinning technique (Kim *et al*. 2008; Thangavel *et al*. 2016) is being used to prepare nanofibers of CuO-PVA and subsequent annealing to remove PVA and then to fabricate nano crystals of CuO. This novel method of synthesis is efficient and simple method of preparing nano particles with high yield at low cost.

2. EXPERIMENTAL DETAILS

2.1 Preparation of precursor solution

The precursor solution of CuO was prepared using the following procedure. 5g of Copper Acetate (Merk grade) and 3 g of NaOH (Merk grade) were weighed using single pan balance (accuracy 0.001 mg) and transferred to agar mortar and grounded one after another for 5min. The obtained fine powders were mixed with 6 ml of PEG 400 (Polyethylene glycol 400) and grinded for 30 min using a mortar. The obtained paste was thoroughly washed with distilled water and then with ethyl alcohol twice to remove the PEG 400 in order to control the size of the nano particles. The paste was dried at 70 ^{o}C in an oven for 2 hours. The resultant solid granules were subsequently annealed at 400 ^{o}C, 500 ^{o}C and 600 ^{o}C in a muffle furnace for 2 hours and cooled to room temperature. The fine powders were mixed with PVA (analytical grade) and preserved separately in different vials. The complete experimental procedure in this research is depicted as flow chart given below (Fig.1).

T. Venkatachalam
email: tvenkatachalam@cit.edu.in

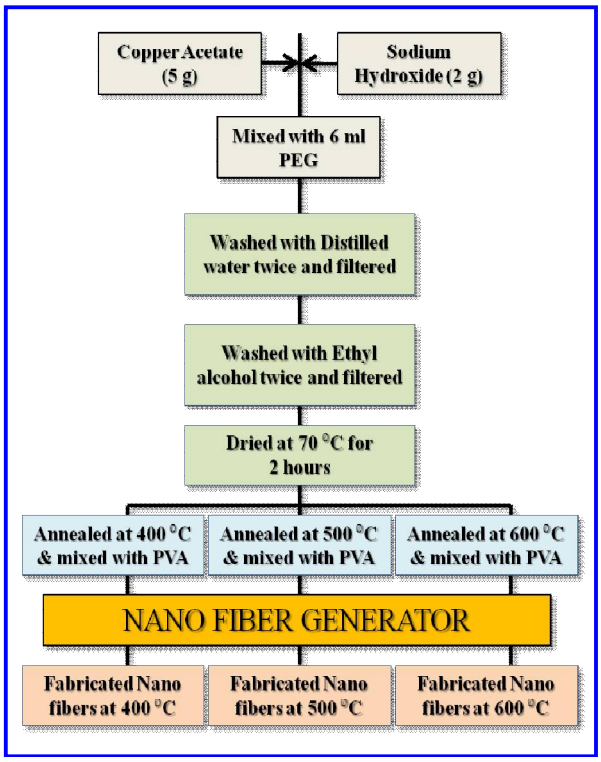

Fig. 1: Flow Chart of the Nanofiber Synthesis

2.2 Nano fiber Generator

The microcontroller based electro spinning nanofiber generating unit was identified, for the preparation of CuO nanofiber in this research. The unit was designed and fabricated using the electronic components in the laboratory as shown in the schematic diagram Fig.2. It consists of three major units i) High voltage power supply (0 to 30 kV), ii) Nano fiber producing unit, and iii). Nano fiber collecting unit. The microcontroller (PIC 16F877A) fitted board was connected with computer and the operating voltage was drawn from the 6V DC power supply unit. Using test solution (appropriate viscous sugar solution) in syringe, the flow of liquid from the tip of the stainless needle was assured. Another similar programmed microcontroller fitted board and the inverter (with potentiometer) are attached along the line output transformer (LOT) and the output terminals were connected across the needle of the syringe and the substrate fitted metal holder to apply high voltage. The expected variation of voltage across the needle and the holder from 1 kV to 30 kV with adjustment of the potentiometer was measured and the potentiometer was calibrated.

2.3 High voltage power supply unit

The variable high voltage power supply unit (microcontroller based) is used to generate 0-30 KV C voltage between the needle and the collecting unit. The fly back transformer transforms energy and also stores energy for a small fraction of the switching period. It has high reluctance of magnetic flux to store energy. In primary and secondary windings the current does not flow simultaneously, the fly back transformer is a freely tied inductor rather than a classical transformer, in which current flow concurrently in all magnetically coupled windings. The primary winding of the fly back transformer is usually driven by a switch from a DC supply. The primary inductance induces the current to build up in a ramp when the switch is turned on. But when the switch is turned off, the current in the primary winding collapse, then as a result of this the voltage in the output windings raises quickly. When the input current in the primary is switched off, an EMF is induced in the secondary and this time diode conducts, as its polarities are different. This induced voltage is then rectified and filtered with a capacitor producing a DC output.

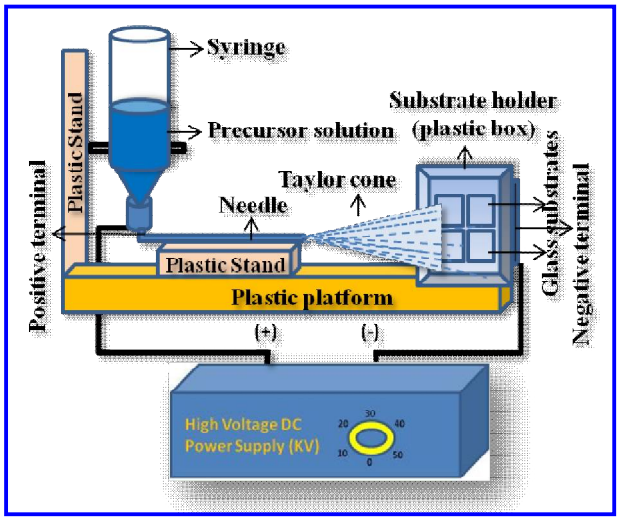

Fig. 2: Schematic Diagram of Nanofiber Generator

2.4 Nano fibber producing unit

The Spinneret solution feeding unit is made up of syringe (with stainless steel needle of size (0.1mm to 0.3 mm). The precursor solution is taken in the vertically mounted plastic syringe with the 'L' shaped metallic needle at the bottom, so that the solution can ooze out as droplets in the tip of the needle by gravity. The diameter of the droplet is equal to the diameter of the needle (0.26 mm). The needle is fitted with positive and the collecting unit is connected to negative of the power supply unit. The collecting unit is having a brass plate pasted on a vertical plastic stand and a thin plastic box without lid is fitted over it with four well cleaned substrates of size 1cm x 1cm. The needle and the collecting unit are placed at same level and 5cm to 8 cm apart. The whole arrangement is placed inside a plastic box, so that the nanofiber could not pollute the outside

the system. Here the applied field is very large, so there is penetration of the electric field is taking place. As soon as the droplet is formed at the tip of the needle, due to electric field, a taylor cone is formed and fibers are deposited on the four glass plates. The plastic boxes with glass substrates were collected after deposition and covered with their lids and labeled for further characterizations.

2.5 Nanofiber collecting unit

Many methods are adopted to collect the generated nanofiber. One of the popular method is by using a flat plate collector which generates nonaligned nanofiber. This is cheaper method of producing nanofibers in the glass plate which is connected to a high voltage negative potential. During nanofiber generation the collector must be grounded or maintained at high negative potential. When a high voltage is applied, the electrostatic force is exerted across the spinneret and the collector. The collector draws the polymer solution from the spinneret in the form of the nanofiber and the generated nanofiber is deposited on the surface of the collector.

2.6 Preparation of CuO nanofibers

The high voltage power supply is mandatory in electro-spinning technology to spawn the nanofibers. Syringe pump, also known as spinnerets, are small pumps precisely operated by its own gravity action. When the prepared nano powders are dissolved in ethyl alcohol and kept in sonicator for 15 min to get a homogeneous solution and then it is filled in the syringe (fiber producing unit). With the help of high voltage, an applied electric field is applied in between the spinneret and collector. The collector draws the polymer solution from the spinneret in the form of nanofibers and the generated nanofibers are then coated on the surface of the collector. Thus the CuO nanofibers are fabricated from micro controller based electro-spinning method.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction Analysis

The Fig.3 shows the X-ray diffraction (XRD) pattern of the CuOnano fiber synthesized from copper acetate and sodium hydroxide by solid state synthesis method. The XRD diffraction studies were carried out for the samples annealed at 400 ^{o}C, 500 ^{o}C and 600 ^{o}C separately. The XRD pattern revealed the orientation and crystalline nature of copper oxide nano fiber. The peak position with 2θ value of 32.50 ^{o}, 38.80 ^{o} and 48.81 ^{o} are indexed as (110), (200), ($\bar{2}$02) planes, which are in good agreement with those of powder CuO obtained from the International Center of Diffraction Data card (JCPDS-895895) conforming the formation of crystalline monoclinic structure. The lattice parameters are a=4.639 Å, b = 3.468 Å and c = 6.241 Å and α = γ =90 ^{o}, β = 99.5 ^{o}.

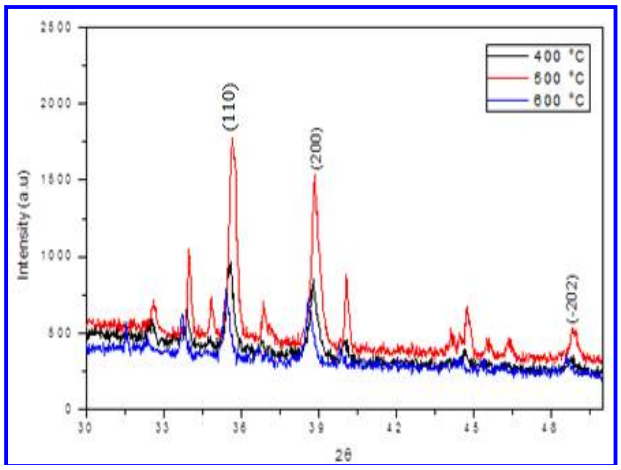

Fig. 3: XRD Pattern of the Nanocrystals

The obtained results are well consistent with the previously reported literature (Langford *et al*. 1991; Abaker *et al*. 2011).The crystalline size (D) is calculated using Scherrer's formula ($D = \frac{0.94\,\lambda}{\beta \cos\theta}$). The full width at the half maximum (β) is calculated for the slope of β Cos θ versus Sin θ plot using the relation$\beta = \frac{\lambda}{D\cos\theta} - \varepsilon \tan\theta$. The dislocation density (δ) is calculated from the relation $\delta = 1/D^2$. The lattice parameters (a, b &c) of the crystals were determined by using the relation

$$\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2\gamma} + \frac{k^2}{b^2 \sin^2\gamma} - \frac{2hk\cos\gamma}{ab\sin^2\gamma} + \frac{l^2}{c^2}$$

Where (hkl) is the Miller indices of the predominant peaks.

3.2 Optical Analysis

UV-Vis-NIR spectroscopy study was carried out on the samples of CuO nano fibres annealed at different temperatures such as 400°C, 500°C and 600 °C. The observed absorbance spectrum shows that the minimum cut-off wavelength of 300 nm, 314 nm and 317 nm respectively. The role of annealing temperature has a considerable effect on the grain size of the particle, where as the crystalline nature increases with respect to increase in its annealing effect. It induces a strain mediated effect on the sample of CuO, which improvises the role of layers leads to the increase in the absorption edge of the sample. The surface trapping effect of grain boundaries, minimizes its effective strength with respect to the annealing, hence there is an increase in its absorption edge. The increasing red shift with decreasing particle size suggests that the defects responsible for the intra-gap states are primarily as

surface defects (Sukhorukov *et al*. 2006; Ovchinnikov *et al*. 2007; Rehman*et al*. 2011) and show higher band gap (Rehman*et al*. 2011; Koffyberg *et al*. 1982). The blue shift in the direct band edges as seen in our case is due to the quantum confinement effect (Rehman *et al*. 2011; Neeleshwar *et al*. 2005).

The absorption coefficient (α) is estimated from the Optical transmittance spectra using the relation $\alpha = 2.303 \log (100T) / t$ where T is the Transmittance (in %) and t is the thickness of the film. All the graphs satisfied the condition for direct transition in the excitation process (**ie**) $\alpha = (E_v\text{-}E_i)^{1/2}$ for allowed direct transition., where E_v is the top of the valence band and E_i the initial state from which the transition is made. The band gap of the nano crystals prepared at three temperatures 400 °C, 500 °C and 600 °C, were determined by extrapolating the curve in the graph drawn between $(\alpha h\gamma)^2$ and $(h\gamma)$. It is found that they are direct band gap semiconductors having 1.95 eV, 2.09 eV and 2.28 eV respectively and their band gap increases with temperature.

3.3 FESEM and EDAX Analysis

The surface morphology and microstructure of pure CuO nano particles were investigated by using Field emission scanning electron microscope (FESEM). As seen in the FESEM images (Fig.4), the crystallites are spherical at low temperature (400 ºC) and are very fine rod like at higher temperatures (500 ºC), then it becomes nano crystalline at 600 ºC. It is also evident that the particle size decreases with increase in annealing temperature, which is consistent with XRD results calculated by Scherrr's equation. The presence of copper and oxide is confirmed in the EDAX spectra (Fig.5) and its molecular formula is CuO.

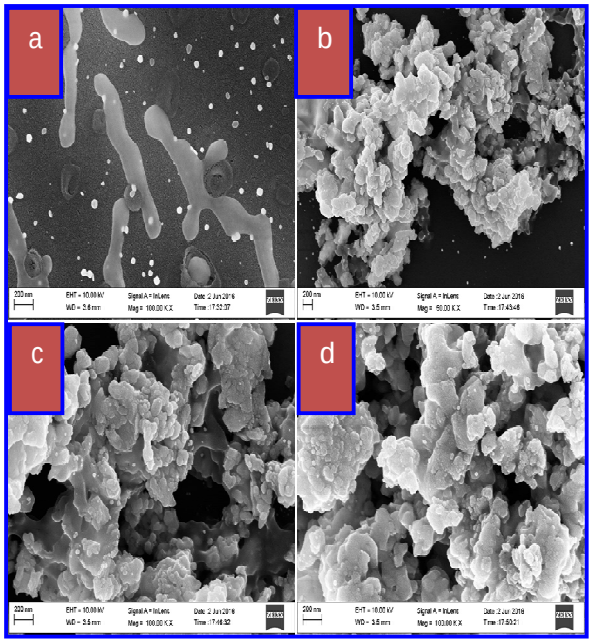

Fig. 4: FESEM images of the nano fibers annealed at a) 400℃ b) 500℃ c) 600℃

Table 1. Lattice parameter, crystalline size, stress, strain and dislocation density of nano crystals

Peak number	Temperature (°C)	(hkl)	2θ (°)	Lattice parameter (Å)	Crystalline Size D (nm)	Stress (Mega Pascal)	Strain 10^{-4}	Dislocation Density $10^{14}(m^{-2})$
1	400	110	35.508	a = 4.636	29.31	185.250	12.350	11.644
2		200	38.806	b = 3.418	22.74	238.785	15.919	19.338
3		$\bar{2}02$	48.819	c = 6.262	23.68	229.365	15.291	17.838
Average values					25.24	217.800	14.520	16.273
1	500	110	35.509	a = 4.628	25.49	212.955	14.198	15.379
2		200	38.878	b = 3.421	22.87	237.495	15.833	19.126
3		$\bar{2}02$	48.901	c = 6.253	26.66	203.655	13.578	14.065
Average values					25.00	218.035	14.54	16.190
1	600	110	31.562	a = 4.654	26.87	205.320	13.688	13.845
2		200	38.645	b = 3.566	22.04	246.311	16.412	22.048
3		$\bar{2}02$	48.852	c = 6.209	23.85	227.564	15.171	17.978
Average values					24.25	226.390	15.09	17.950

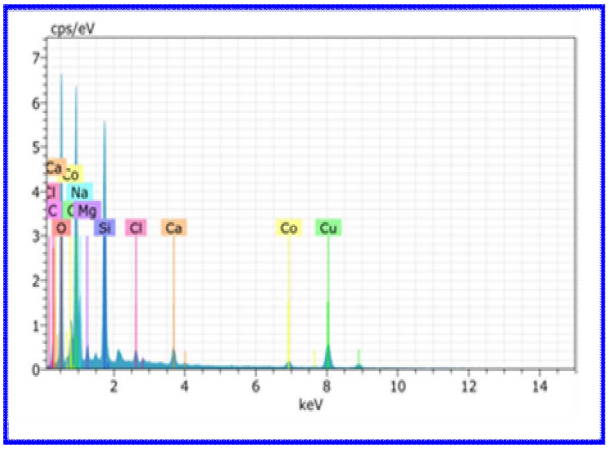

Fig. 5: EDAX Spectra of fabricated CuO nano fibers after annealing

4. CONCLUSION

The nano crystals of CuO with monoclinic structure have been synthesized through a simple, low cost solid state reaction method. It has been noticed that improved crystallinity was observed when annealed at higher temperatures. The intensity of peaks has been increased with increase in annealing temperature. The optical studies show CuO is the direct band gap semiconductor and the band gap decreases with increase in temperature. The FESEM results confirm the formation of nano crystals precisely at higher annealing temperatures. Also the EDAX results confirm the existences of CuO nano particles.

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